

Methanol Permeability and Properties of DMFC Membranes Based on Sulfonated PEEK/PVDF Blends

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ABSTRACT: Proton exchange membranes for a direct methanol fuel cell were prepared by blending poly(vinylidene fluoride) [PVDF] with sulfonated poly(etheretherketone) [SPEEK]. The effects of PVDF content on methanol permeability in the blend membranes were investigated by using a diffusion cell and gas chromatography technique. The thermal resistance and proton conductivity of the membranes were also determined by using a thermal gravimetric analysis (TGA) and an impedance analysis technique, respectively. It was found that methanol permeability in the blend membranes decreased with PVDF

content at the expense of proton conductivity. The methanol permeability values of the blend membranes are much lower than that of Nafion 115, whereas proton conductivities of the membranes are comparable to that of Nafion. The thermal stability of these blend membranes are above 250°C which is sufficiently high for use in DMFC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5941–5947, 2006

Key words: ion exchangers; polyelectrolytes; ionomers; membranes; blends

INTRODUCTION

A direct methanol fuel cell (DMFC) is a kind of proton exchange membrane fuel cell (PEMFC), which utilizes methanol as a fuel to generate electricity without the use of any reforming unit. In the DMFC, methanol is oxidized at the anode, generating electrons, protons, and carbon dioxide. The proton is transported through the polymeric electrolyte membrane from the anode to the cathode and then combined with oxygen and electron to complete the redox reaction. Consequently, electricity is generated with water being a by-product (see Fig. 1).

Normally, for a proton exchange membrane fuel cell utilizing hydrogen as fuel, perfluorinated polymers containing sulfonate groups such as Nafion is often used as an electrolyte polymeric membrane. This is due to the fact that the Nafion[®] has a very high proton conductivity, good thermal resistance, and chemical stability. However, the Nafion membrane still has some disadvantages, especially when it is to be used in DMFCs. The first problem is methanol crossover, which is a diffusion of methanol through the electrolyte membrane from anode to cathode, causing loss of

fuel. It was reported that about 40% of the methanol was lost through the process called “methanol crossover.”¹ Furthermore, the presence of methanol in the cathode side reduced the cathode voltage and efficiency of the fuel cell. Besides the crossover problems, the Nafion membrane also has some other disadvantages such as the considerably high cost of the material and a decrease in proton conductivity at an operating temperature above 100°C because of loss of water.² Therefore, several efforts have been made to develop new electrolyte polymeric membranes that can be used as an alternative membrane for DMFCs. Examples of polymeric membranes which have been developed for use in DMFCs include sulfonated poly(vinyl alcohol),³ polystyrene sulfonic acid crosslinked within a poly(vinylidene fluoride) matrix,⁴ and sulfonated poly(etherether ketone).⁵

Rhim et al.³ for example, modified polyvinyl alcohol [PVA] by reacting it with some sulfonating agents such as sulfoacetic acid and sulfosuccinic acid. The proton conductivity of the resulting PVA membrane was improved after the sulfonation. The thermal stability of the sulfonated PVA membrane is about 150°C, which is higher than the normal operating temperature of the DMFC (about 90–120°C).⁶ However, further development of DMFC membranes with higher thermal stability is still challenging and desirable. It was recommended⁷ that operating the proton exchange membrane fuel cell at a temperature of 140°C would be an advantage because in this temperature range, anode catalyst poisoning by CO is less important, the kinetics of fuel oxidation will be improved

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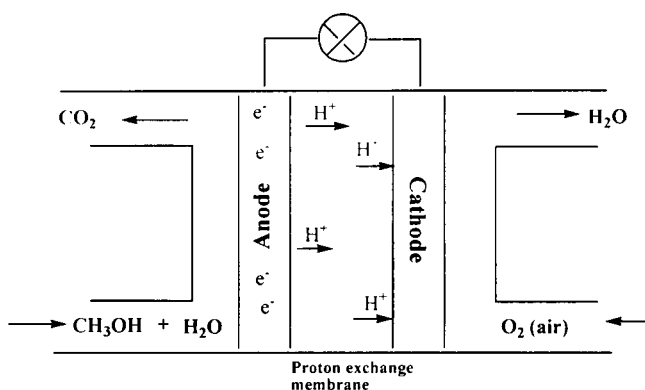


Figure 1 Schematic principle of a direct methanol fuel cell (DMFC).

and the efficiency of the cell significantly enhanced. Besides the thermal stability, the chemical degradation of the sulfonated PVA membrane via hydrolysis under DMFC operating condition is still doubtful.

Alternatively, polymers containing an aromatic backbone such as polystyrene (PS) and poly(etheretherketone), [PEEK] might be considered. These polymers can be sulfonated through the use of some sulfonating agents such as conc. sulfuric acid,⁸ chlorosulfonic acid,⁹ and trimethyl silyl ester.¹⁰ The reaction proceeds via a direct electrophilic sulfonation mechanism and the sulfonate groups attach to the aromatic rings of the polymer backbone. The properties of the sulfonated polystyrene have been studied.¹¹ The proton conductivity of the membranes increased with the degree of sulfonation at the expense of methanol resistance. Besides this, the membranes tended to be chemically degraded in the presence of peroxide intermediates, which were produced from a reduction of oxygen at the cathode. These intermediates are capable of attacking the tertiary hydrogen at the α -carbon of the sulfonated PS, resulting in losses of the aromatic ring and sulfonate groups.¹² However, by blending with a partially fluorinated polymer such as poly(vinylidene fluoride) [PVDF] in a form of a semi-interpenetrating polymer network (sIPN),¹³ degradation of the sulfonated PS membrane can be prolonged. More interestingly, the methanol crossover of the sIPN membrane decreased when compared with that of Nafion 117. This result suggests that the blending of sulfonated polymers with PVDF is an interesting strategy for improving methanol resistance of the DMFC membrane.

Apart from the sulfonated PS membranes, poly(etheretherketone) [PEEK] is an interesting material, which should be considered for further development for use in DMFC. PEEK is mechanically strong and resistant to high temperatures of up to 300°C. The proton conductivity of the material can be chemically modified by reacting it with sulfonating agents such as sulfuric acid.⁵ As a result, modified PEEK with sulfonic groups attached to the aromatic ring of the main

chains was obtained. The degree of sulfonation (DS) of the modified polymer can be varied by adjusting the reaction conditions such as the reaction time and reaction temperature. Properties of sulfonated poly(etheretherketone) [SPEEK] membranes in relation to DMFC were studied¹⁴ and it was found that the proton conductivity of SPEEK increased with the DS at the expense of methanol resistance. The methanol resistances of the SPEEK membranes are yet to be enhanced, even though the crossovers are considerably lower than that of Nafion. This is because the lower the methanol crossover, the better the fuel cell efficiency. Some efforts have been made to reduce the methanol crossover of the sulfonated PEEK membranes. For example, by mixing with nanofillers such as silica¹⁵ and organic-montmorillonite (OMMT).¹⁶ It was found that methanol resistance of these nanocomposite SPEEK membranes increased at the expense of proton conductivities.

In this study, the methanol permeability of membranes based on sulfonated PEEK blended with poly(vinylidene fluoride), [PVDF], is of interest. PVDF is mechanically strong and tough. In addition, it was believed that PVDF is inherently resistant to methanol crossover because of the hydrophobic nature of the material. Therefore, by blending PVDF with sulfonated PEEK, a membrane with optimum proton conductivity and methanol resistance can be expected. The aim of this study is to investigate the effects of blending ratios on water uptake, ion exchange capacity, proton conductivity, methanol permeability, and the thermal properties of sulfonated PEEK/PVDF blend membranes.

EXPERIMENTAL

Materials

Poly(etheretherketone) (PEEK, VICTREK 150PF) was purchased from Victrek (Lancashire, UK), Poly(vinylidene fluoride), [PVDF, $M_w = 530,000$] was supplied from Fluka. Sulfuric acid (analytical grade from Merck, Darmstadt, Germany), propionic anhydride (purum grade from Fluka, Buchs, Switzerland), methanol (analytical grade obtained from Fisher Chemicals, Loughborough, UK), and dimethyl formamide (DMF, analytical grade from Univar, Seven Hills, NSW, Australia), were used as received.

Sulfonation of PEEK

About 6 g of the dried PEEK powder was carefully added to 200 mL of conc. sulfuric acid (95–97%) at an ambient temperature in a reaction flask under vigorous stirring. The actual temperature in the reaction flask was 35°C. Changes in the color of the solution from colorless to light brown and finally dark brown were noted within a few minutes, indicating the progress of the sulfonation. The reaction was kept stirring

at room temperature for further 48 h. After that, the reaction was terminated by slowly dropping into ice-cold de-ionized water under continuous stirring. The precipitated polymer was filtered and washed with de-ionized water until pH = 6. The polymer was then dried in a vacuum oven at 70°C for 12 h.

Membrane preparation

Two separate solutions of sulfonated poly(etheretherketone), (SPEEK) and PVDF were prepared by using dimethyl formamide (DMF) as a solvent. To obtain the solution blend at the desired ratio, a suitable quantity of PVDF solution was added to the SPEEK solution and stirred at room temperature for further 30 min. The concentration of the blend solution was kept constant at 10% w/v solution. A suitable amount of the solution was then cast onto a clean glass substrate before drying in an oven at 110°C for 1 h to obtain a ~ 50- μ m thick membrane. After that, the membrane was peeled off from the substrate and then dried in a vacuum oven at 70°C for further 12 h to remove any residual solvent. The membrane was kept in de-ionized water before tests.

Characterizations

The chemical structure of the modified PEEK was determined by both ¹H NMR and ¹³C NMR techniques using a Bruker Advance DPX 400 NMR spectrometer at 20°C, using deuterated dimethyl sulfoxide (DMSO-d₆) as a solvent. The chemical shift of tetramethylsilane (TMS) was used as internal standard reference.

The thermal stability of the SPEEK/PVDF blend membranes was examined by using a Thermogravimetric analyzer (TGA, NETZSCH STA 409 C/CD). About 20 mg of the sample was used. The TGA experiment was scanned over temperatures ranging between 25 and 1000°C under oxygen (air) atmosphere, at a heating rate of 20°C/min.

Water uptake

The measurement of water uptake of the sulfonated PEEK/PVDF blend membrane was conducted by immersing the membrane into de-ionized water at 25°C for 24 h. After that, the water-swollen membrane was taken out, wiped with tissue paper, and immediately weighed. The water uptake (W) was then calculated from the following equation:

$$W (\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weight of dry and water-swollen membranes, respectively.

Ion exchange capacity

The ion exchange capacity (IEC) of the membrane was determined by titration. The membrane was

immersed in 10 mL of 0.1M NaCl solution for 24 h to exchange protons with sodium ions.¹⁷ After that, the IEC value was determined by carrying out a back titration of the solution with 0.1M NaOH to evaluate the released amount of protons, using phenolphthalein as an indicator. The IEC value was calculated by using the following equation:

$$\text{IEC} = [M_{E, \text{NaOH}}]/W_{\text{dry}} \quad (2)$$

where $M_{E, \text{NaOH}}$ is the mol equivalent (meq) of NaOH and W_{dry} is the weight of the dry membrane (g).

It is worth mentioning that the methods described earlier might be slightly different from those described in some literature, in terms of the chemicals used.¹⁴ In the latter case, the SPEEK was immersed in NaOH solution for 1 day before being back titrated with HCl. In this study, however, an immersion of the SPEEK/PVDF blend in the NaOH solution for 24 h was avoided because poly(vinylidene fluoride) can be dehydrofluorinated by treating with alkaline.¹⁸ Consequently, the membrane could be degraded and the titration result could be misleading.

Methanol permeability

The resistance to methanol crossover of the membrane was evaluated by measuring the methanol permeability of the membrane. A two-identical-compartment glass cell was used as a diffusion cell for the measurement. The membrane was placed between the two compartments and then clamped. After that, 20 mL of methanol solution (2M) and 20 mL of de-ionized water were filled in compartments A and B of the cell, respectively. Both compartments were magnetically stirred at room temperature during the permeation experiments. The concentration of methanol in compartment B was measured as a function of diffusion time by using a gas chromatography (GC) technique with a FID detector (Agilent, containing porapak QS column). The injection temperature and the column temperature used for the GC experiment were 220 and 150°C, respectively. The area under the methanol peak from each GC chromatogram was used in combination with a calibration curve to determine the methanol concentration. Finally, the methanol permeability was calculated from the slope of the plot between the methanol concentration and diffusion time, using the following equation:

$$C_B(t) = A(DK)C_A(t - t_0)/V_B L \quad (3)$$

where C_A and C_B are the concentration of methanol in compartments A and B and V_A and V_B are the volumes of liquids in compartments A and B, respectively. A and L are the area and thickness of the mem-

brane, and D and K are the methanol diffusivity and partition coefficient, respectively. The product of DK is the membrane permeability.

Proton conductivity measurement

The proton conductivities of the membranes were measured by using a four-point probe technique. The impedance of the membranes was measured by using an impedance analyzer (Autolab, PGSTAT 30) at a frequency of 10.0 kHz. The membranes were cut into $3 \times 3 \text{ cm}^2$ strips and immersed in de-ionized water for 12 h, before the measurement. The hydrated membrane was mounted onto the cell and an AC current of 0.35 mA was applied to the cell. The conductance of the sample was obtained from the AC potential difference between the two inner electrodes. The conductivity (σ) was calculated by using the following equation:

$$\sigma = l/RS \quad (4)$$

where σ is the proton conductivity (S/cm), R is the bulk resistance of the membrane, S is the cross-sectional area of the membrane (cm^2), and l is the distance between the counter electrode and the working electrode (cm).

RESULTS AND DISCUSSION

Characterizations of the sulfonated poly(etheretherketone)

Figure 2 shows a ^{13}C NMR spectrum of the sulfonated poly(etheretherketone), (SPEEK). The sulfonation oc-

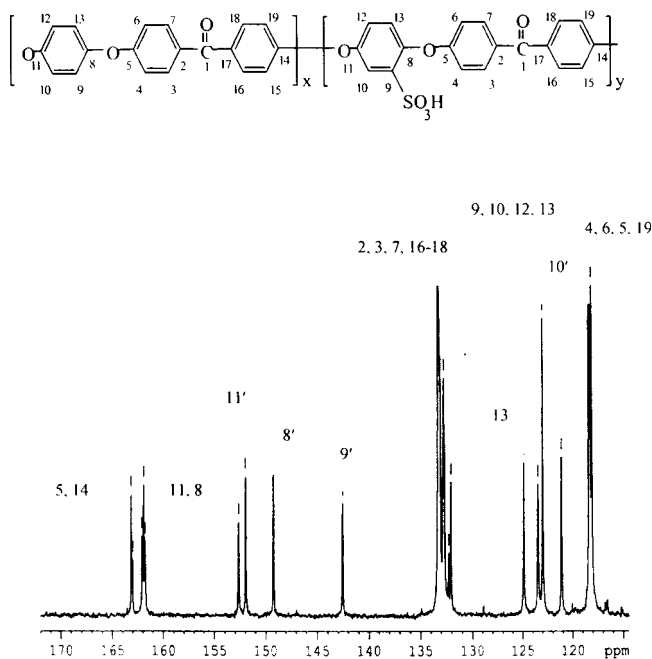


Figure 2 ^{13}C NMR spectrum of sulfonated poly(etheretherketone).

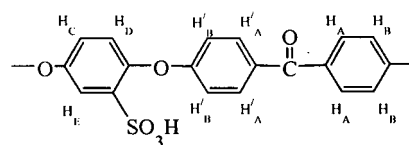


Figure 3 ^1H NMR spectrum of sulfonated poly(etheretherketone).

curred exclusively on the hydroquinone segment because sulfonation of PEEK in sulfuric acid is an electrophilic substitution reaction. The sulfonic groups can be introduced into the hydroquinone segment of the polymer chain activated for electrophilic substitution by the ether linkage. On the other hand, the presence of the carbonyl group would deactivate the other two phenyl rings connected through the ether linkages by the electron-withdrawing effect.

To determine the degree of sulfonation (DS) of SPEEK, ^1H NMR spectrum of the modified polymer should be considered (Fig. 3). All four H_A appears at low field because of the de-shielding effect of the carbonyl group. The two H_B protons located at 7.03 ppm shifted upward by the proximity of the electron rich SO_3H group, whereas the remaining $\text{H}_{B'}$ protons absorb at 7.15 ppm. The presence of the sulfonic group caused a significant down field shift of the hydrogen signals in the hydroquinone ring from 7.22 (H_C) and 7.12 ppm (H_D) to 7.52 ppm (H_E). In this regard, the intensity of the H_E signal might be used for an estimation of the H_E content which is equivalent to the sulfonic group concentration. The DS value can be derived from the ratio between the peak area of the H_E signal (AH_E) and the integrated peak area of the signals corresponding to all other aromatic hydrogens ($\text{AH}_{A,A',B,B',C,D}$), using the following equation:

$$\text{DS}/(12 - 2\text{DS}) = \text{AH}_E / \sum (\text{AH}_{A,A',B,B',C,D}) \quad (5)$$

From the calculation using the above equation, the DS value of the SPEEK obtained from this study is 0.78. This value is different from that reported by Ye et al.,¹⁹ who prepared SPEEK by reacting with H_2SO_4 at room temperature. The difference, however, could be attributed to the fact that the reaction time and concentration of the PEEK in acid solution were dif-

ferent. In addition, the DS value of the SPEEK in this study is higher than that was reported by Xing et al.⁵ for the SPEEK sulfonated by using the similar PEEK/ H_2SO_4 ratio (40 g of the PEEK in 1400 mL of the sulfuric acid) for 60 h. Again, the difference could be attributed to the different reaction condition i.e., the sulfonation temperature reported by Xing et al.⁵ was 22°C, whereas the actual reaction temperature in this study was 35°C.

No further attempts are made herein to prepare and study the SPEEK with different DS values. According to our experience, SPEEK with a very low DS value, such as that obtained by reducing the reaction time from 48 to 24 h, was not completely soluble in DMF and that could inhibit the solution blending and membrane casting process. On the other hand, SPEEK with a very high DS value tended to be soluble in water. This means that removing some residual acid from the SPEEK product by washing with de-ionized water would be very difficult. The SPEEK yield obtained from the washing and filtration process is usually lower than expected, unless some other separation technique such as dialysis is employed. Furthermore, very high water uptake of the SPEEK membrane might promote more methanol crossover through the membrane, which is undesirable. Therefore, the SPEEK with a DS value of 0.78 obtained from this study is considerably qualified and suitable for blending with PVDF for further study.

Thermal properties of SPEEK/PVDF membranes

Figure 4 shows a TGA thermogram of a SPEEK/PVDF membrane (30/70% w/w). The initial weight loss at about 80–100°C is because of water loss. The second transition occurring over the temperature

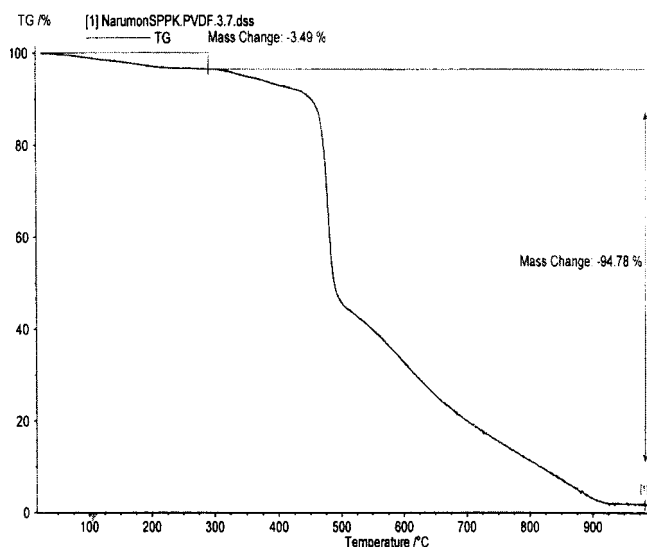


Figure 4 TGA thermogram of SPEEK/PVDF blend membrane (30/70% w/w).

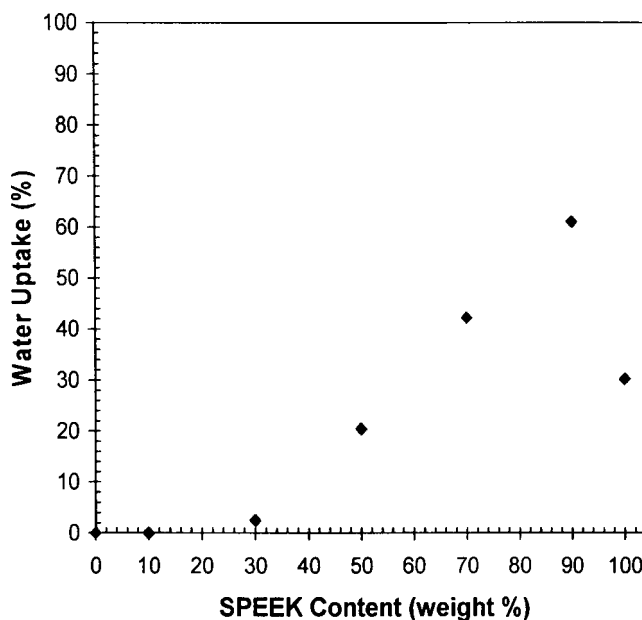


Figure 5 Water uptake values of various SPEEK/PVDF blend membranes.

range from 270 to 500°C is attributed to a loss of sulfonic groups (desulfonation) in SPEEK.²⁰ The third weight loss occurred over the temperature range between 400 and 500°C and could be ascribed to the decomposition of PVDF molecules.²¹ This was in a good agreement with our observation noting that the percentage mass change of this transition decreased with decreasing PVDF content. Finally, the fourth transition, occurring over the temperature range between 500 and 900°C, could be related with decomposition of the SPEEK main chain. Again, the percentage mass change of this transition increased with the SPEEK content. For the SPEEK/PVDF membranes with different blending ratios, their TGA thermograms also show a similar profile in terms of transition temperatures. These SPEEK/PVDF membranes are stable up to 250°C, which is far above a normal operating temperature of DMFC (about 90–120°C).⁶ The results indicate that the thermal stabilities of these SPEEK/PVDF membranes are sufficiently high to meet the requirements of DMFC.

Water uptake, ion exchange capacity (IEC), and proton conductivity

Figure 5 shows water uptake values of various SPEEK/PVDF membranes. It can be seen that the membranes containing less than 50% SPEEK scarcely have any water uptake. This could be ascribed to the fact that these membranes contain high amounts of PVDF material, which is inherently hydrophobic. However, as the SPEEK content was increased from 50 to 90%, the water uptake values increased. This was accompanied

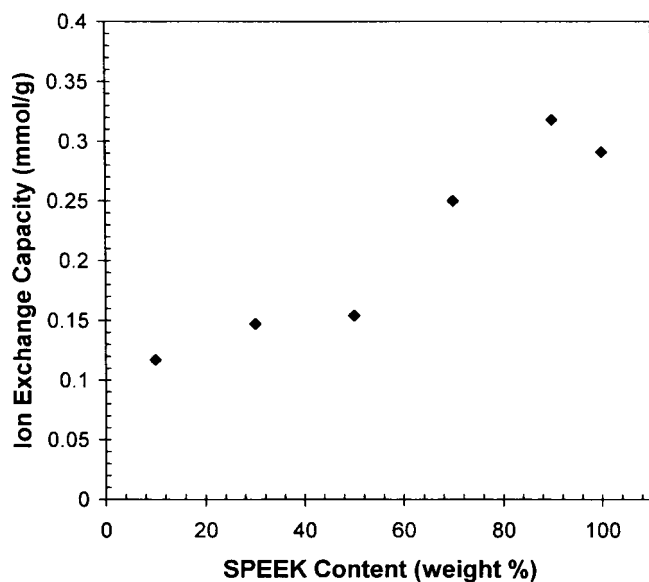


Figure 6 Ion exchange capacities (IEC) of various membranes.

by our observation noting that the physical appearance of the membranes changed from a PVDF rich matrix to a SPEEK rich matrix. The water uptake of the pure SPEEK membrane was about 30%. This is very close to that of a literature value⁵ of SPEEK with a comparable DS (DS determined by ¹H NMR = 0.79). Notably, in this study, it was found that the water uptake of the pure SPEEK is lower than that of the SPEEK/PVDF blend membranes containing 70 and 90% by weight of SPEEK. In our opinion, this effect could be attributed to the fact that PVDF is totally hydrophobic, whereas SPEEK is highly hydrophilic. Consequently, the two polymers tend to be immiscible.²¹ Phase separation within a microstructure of the blend might create a larger "water channel," allowing more water uptake.

In general, high water uptake is a prerequisite for a good proton-conducting membrane because water would induce a dissociation of the protons from SO₃H groups and would also act as "vehicles" for the transportation of the protons from the anode to the cathode.²² In relation to this study, only the blend membranes containing high SPEEK content (50, 70, and 90% by weight SPEEK) were used for further

study on proton conductivity because water uptakes of the blend membranes containing 10 and 30% of SPEEK range between 0 and 3% which is very low.

The ion exchange capacity (IEC) values of various membranes are shown in Figure 6. The IEC values of the blend membranes continuously decrease with decreasing SPEEK content, owing to the fact that the PVDF lack of sulfonate groups contributing to the ion exchange process. Again, the ion exchange capacities (IEC) of these blend membranes containing 10 and 30% SPEEK (Fig. 6) were relatively low, implying that proton conductivity of the blend membranes could be very low.

Table I compares the proton conductivities of various membranes. The proton conductivity of a pure SPEEK membrane is about 10.34×10^{-3} S/cm, which is comparable to that of a Nafion115 membrane (10.5×10^{-3} S/cm) measured by using the same apparatus and testing conditions. When the SPEEK was blended with PVDF, the proton conductivity of the membranes gradually decreased with PVDF content. This is due to the fact that PVDF lack sulfonic groups. As a result, the higher the PVDF content, the lower the proton conductivity of the membrane.

Methanol permeability

Finally, the methanol permeability of various membranes was determined and the results are illustrated in Table II. It can be seen that, although the methanol permeability of the pure SPEEK membrane is considerably lower than that of the Nafion115 membrane, further improvement can be made by blending with PVDF. The methanol permeability of the SPEEK membrane rapidly decreased by two orders of magnitude after SPEEK was blended with 10 and 30% by weight PVDF. For the blend membranes which contain more than 30% by weight of PVDF, a methanol peak in a GC chromatogram was absent, indicating that there was no methanol crossover through the membranes. It was believed that this is attributed to the hydrophobic nature of PVDF which restricts methanol solubility in the PVDF rich membranes.

TABLE I
Proton Conductivity Values of Various Membranes

Membranes	Proton conductivity (10^{-3} S/cm)
SPEEK/PVDF (50/50)	7.18
SPEEK/PVDF (70/30)	9.10
SPEEK/PVDF (90/10)	8.99
SPEEK	10.34
Nafion 115	10.50

TABLE II
Methanol Permeability of Various Membranes

Membranes	Methanol permeability (cm^2/sec)
PVDF	No methanol crossover
SPEEK/PVDF (10/90)	No methanol crossover
SPEEK/PVDF (30/70)	No methanol crossover
SPEEK/PVDF (50/50)	No methanol crossover
SPEEK/PVDF (70/30)	5.34×10^{-9}
SPEEK/PVDF (90/10)	5.66×10^{-9}
SPEEK	2.35×10^{-7}
Nafion 115	3.39×10^{-7}

CONCLUSIONS

This work has shown that the methanol crossover of a sulfonated polymer such as SPEEK could be effectively reduced by blending with PVDF. The methanol resistance of the SPEEK/PVDF membranes increased with the PVDF content at the expense of their ion exchange capacities and proton conductivities. The optimum blending ratios for SPEEK/PVDF membranes, which provide compromised proton conductivity and methanol permeability, ranged between 50/50 and 90/10% w/w. These membranes are potentially useful to serve as proton exchange membranes in DMFC.

References

1. Narayanan, S. R.; Kindler, A.; Jeffries-Nakamura, B.; Chun, W.; Frank, H.; Smart, M.; Valdez, T. I.; Surampudi, S.; Halpert, G.; Kosek, J.; Cropley, C. In Proceedings of the 11th Annual Battery Conference on Applied Advances; 1996; p 113.
2. Staiti, P.; Arico, A. S.; Baglio, V.; Lufrano, F.; Passalacqua, E.; Antonucci, V. *Solid State Ionics* 2001, 145, 101.
3. Rhim, J. W.; Park, H. B.; Lee, C. S.; Jun, J. H.; Kim, D. S.; Lee, Y. M. *J Membr Sci* 2004, 238, 143.
4. Prakash, G. K. S.; Olah, G. A.; Smart, M. C.; Narayanan, S. R.; Wang, Q. J.; Surampudi, S.; Halpert, G. U.S. Pat. 6,444,343 (2002).
5. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K.; Kaliaguin, S. *J Membr Sci* 2004, 229, 95.
6. Neergat, M.; Friedrich, K. A.; Stimming, U. In *Handbook of Fuel Cells*, Vol. 4; Vielstich, W.; Lamm, A.; Gasteiger, H. A., Eds.; Wiley: Milan, 2003; Chapter 63.
7. Savadogo, O. *J Power Sources* 2004, 127, 135.
8. Rehahn, M.; Schlüter, A. D.; Wegner, G. *Die Makromol Chem* 1990, 191, 1991.
9. Nolte, R.; Ledjeff, K.; Bauer, M.; Mülhaupt, R. *J Membr Sci* 1993, 83, 211.
10. Dimitrova, P. G.; Baradie, B.; Foscallo, D. *J Membr Sci* 2001, 185, 59.
11. Carretta, N.; Tricoli, V.; Picchioni, F. *J Membr Sci* 2000, 166, 189.
12. Yu, J.; Yi, B.; Xing, D.; Liu, F.; Shao, Z.; Fu, Y. *J Power Sources* 2002, 4937, 1.
13. Surya Prakash, G. K.; Smart, M. C.; Wang, Q. J.; Atti, A.; Pleyne, V.; Yang, B.; Mcgrath, K.; Olah, G. A.; Narayanan, S. R.; Chun, W.; Valdez, T.; Surampudi, S. *J Fluorine Chem* 2004, 125, 1217.
14. Li, L.; Zhang, J.; Wang, Y. *J Membr Sci* 2003, 226, 159.
15. Karthikeyan, C. S.; Nunes, S. P.; Prado, L. A. S. A.; Ponce, M. L.; Silva, H.; Ruffmann, B.; Schulte, K. *J Membr Sci* 2005, 254, 139.
16. Gaowen, Z.; Zhentao, Z. *J Membr Sci* 2005, 261, 107.
17. Vetter, S.; Ruffmann, B.; Buder, I.; Nunes, S. P. *J Membr Sci* 2005, 260, 181.
18. Kise, H.; Otaga, H. *J Polym Sci Polym Chem Ed* 1983, 21, 3443.
19. Ye, G.; Janzen, N.; Goward, G. R. *Macromolecules* 2006, 39, 3283.
20. Xue, S.; Yin, G. *Eur Polym J* 2005, 42, 776.
21. Chen, N.; Hong, L. *Polymer* 2004, 45, 2403.
22. Kreuer, K. D. *Chem Mater* 1998, 8, 610.